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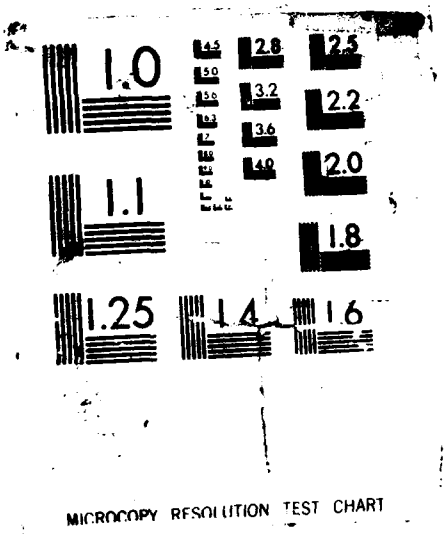

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Topological Aspects of Infinite Metal Clusters and Superconductors

by

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TOPOLOGICAL ASPECTS OF INFINITE METAL CLUSTERS AND SUPERCONDUCTORS

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ABSTRACT

This paper summarizes the chemical bonding topology of infinite metal clusters as well as superconductors constructed from metal octahedra or metal tetrahedra. The chemical bonding topologies of discrete octahedral metal clusters can be either edge-localized (e.g., $Mo_6X_8L_6^{4+}$ derivatives), face-localized (e.g., $Nb_6X_{12}L_6^{2+}$ derivatives), or globally delocalized (e.g., $Zr_6(\mu_2\text{-}Cl)_{12}ECl_{n-12}$ derivatives where E = Be, B, C, N). Infinite fusion of metal octahedra in one, two, and three dimensions leads to metal cluster chains (e.g., Gd_2Cl_3), metal cluster sheets (e.g., ZrCl), and bulk metals, respectively. Superconductors exhibiting relatively high critical temperatures and magnetic fields are constructed from edge-localized metal polyhedra such as the Mo_6 octahedra in the ternary molybdenum chalcogenides (Chevrel phases) and Rh_4 tetrahedra in the ternary lanthanide rhodium borides leading naturally to the concept of porous delocalization in such materials.

INTRODUCTION

The basic building blocks of metal clusters[1] are metal polyhedra, particularly metal deltahedra in which all of the faces are triangles. Initial theoretical work[2-15] focussed on the structure and bonding in discrete metal polyhedra. Subsequent papers[16-21] have treated various aspects of the fusion of metal cluster polyhedra. This paper extends our graph theory derived methods[2-5] to the infinite fusion of metal cluster octahedra. Such infinite fusion in one dimension leads to chains, in two dimensions leads to sheets, and in three dimensions leads to the bulk metals themselves. This work thus provides a novel background for the study of the relationship between discrete metal clusters and bulk metals. In addition such an approach is relevant to the properties of extended solids, particularly properties related to metal-metal interactions such as superconductivity.[22] This paper illustrates the last point by reviewing the bonding topologies in the ternary molybdenum chalcogenides (Chevrel phases) and ternary lanthanide rhodium borides, which represent two types of solids exhibiting relatively high superconducting critical temperatures and/or critical magnetic fields. The bonding topologies of such superconductors are characterized by porous infinite delocalization.[23,24]

BACKGROUND

The chemical bonding topology can be represented by a graph in which the vertices correspond to atoms or orbitals participating in the bonding and edges correspond to bonding relationships. The eigenvalues x of the adjacency matrix of such a graph are related to the Hückel theory molecular orbital energies E and the Hückel parameters α, β and S by the following equation[2,3,4,5,21,25,26]:

$$E = \frac{\alpha + x\beta}{1 + xS} \tag{1}$$

Positive and negative eigenvalues x thus correspond to bonding and antibonding orbitals, respectively.

The two extreme types of chemical bonding in metal clusters may be called edge-localized and globally delocalized.[2,4,5] An intermediate degree of delocalization called face-localized is also possible in certain cases. An edge-localized polyhedron has two-electron two-center bonds along each edge of the polyhedron and is favored when the numbers of internal orbitals of the vertex atoms match the vertex degrees. A face-localized deltahedron has two-electron three-center bonds in each (triangular) face of the deltahedron and can arise when the number of internal orbitals of each vertex atom matches the number of faces meeting at the vertex. A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and is favored when the numbers of internal orbitals match neither the numbers of edges nor the numbers of faces meeting at the vertices. Edge-localized, face-localized, and globally delocalized bonding are all possible in octahedral early transition metal clusters in which the number of internal orbitals from each vertex atom can be either three or four.

One of the major achievements of the graph theory derived approach to the chemical bonding topology in globally delocalized systems is the demonstration of the close analogy between the bonding in two-dimensional planar polygonal aromatic systems such as benzene and that in three-dimensional boranes and carboranes based on deltahedra without tetrahedral chambers.[2,3,4,21] In both cases the three internal orbitals from each vertex are partitioned into two twin internal orbitals and a single unique internal orbital. In the two-dimensional planar polygonal systems the twin internal orbitals overlap pairwise to form the so-called σ-bonding network around the circumference of the polygon and the unique internal orbitals overlap cyclically (C_n graph) to form the so-called π-bonding network. In the three-dimensional deltahedral systems the twin internal orbitals overlap pairwise in the surface of the deltahedron and the unique internal orbitals form a multicenter core bond (K_n graph) at the center of the deltahedron.

The globally delocalized deltahedra with n vertices have 2n + 2 skeletal electrons with 2n of these electrons involved in the surface bonding and the remaining two electrons occupying the single bonding molecular orbital arising from the multicenter core bond.[2,3,4,21] Thus a globally delocalized octahedron has (2)(6) + 2 = 14 skeletal electrons. Electron-rich polyhedra with more than 2n + 2 apparent skeletal electrons have one or more non-triangular faces whereas electron-poor deltahedra with less than 2n + 2 apparent skeletal electrons have one or more tetrahedral chambers. Such electron-poor deltahedra may alternatively be constructed from a smaller deltahedron having no tetrahedral chambers by face-sharing fusion with one or more tetrahedra corresponding to the individual tetrahedral chambers. Thus a capped octahedron can be constructed by fusing an octahedron to a tetrahedron by sharing a triangular face. The electron-poor deltahedra with tetrahedral chambers can thus be regarded as the simplest examples of polyhedral fusion. Conversely, the early transition metal clusters based on infinite fusion of metal octahedra may be viewed as extreme examples of such electron poverty. Such systems thus are appropriately constructed with early transition metals which have relatively small numbers of valence electrons.

The general approach for considering metal cluster bonding models involves calculating the number of available skeletal electrons for comparison with the numbers of skeletal electrons required to fill the bonding molecular orbitals for various cluster shapes and bonding topologies. Difficulties can arise from uncertainties in the valence orbital manifolds and hence the electronic configurations of the vertex atoms or in the partition of the vertex atom orbitals between internal orbitals participating in the skeletal bonding and external orbitals participating in bonding external to the clusters. Such difficulties can sometimes lead to ambiguities in the assignments of bonding topologies in metal clusters in cases where two or more different skeletal bonding topologies assign reasonable electron configurations to the vertex atoms and use all of the available orbitals and electrons. Such ambiguities arise relatively rarely in the treatment of discrete metal clusters but occur more frequently in infinitely fused metal clusters. In addition highly conducting infinite metal clusters may not have enough skeletal electrons to fill all of the bonding orbitals so that there are partially filled conduction bands. These ambiguities limit the applicability of graph theory derived methods for the study of the bonding topology of infinitely fused metal clusters with the difficulties apparently increasing with the number of dimensions of infinite fusion. Nevertheless, ideas which lead to satisfactory bonding models for discrete metal clusters appear to give consistent results for infinitely fused metal clusters.

The early transition metal clusters treated in this paper contain halogen or chalcogen atoms which are either edge-bridging (e.g., μ_2-Cl or μ_2-S) or face-bridging (e.g., μ_3-Cl or μ_3-S) through two or three electron pairs, respectively. Neutral edge-bridging and face-bridging halogen atoms are net donors of three and five electrons, respectively. Similarly, neutral edge-bridging and face-bridging chalcogen atoms are net donors of two and four electrons, respectively. In the actual three-dimensional structures the electron pairs of halogen and chalcogen atoms not required for the primary bridging within a cluster octahedron or chain of octahedra may be donated to adjacent octahedra or chains of octahedra. Such electron pairs from external halogen or chalcogen atoms must be considered in electron-counting schemes in order to obtain meaningful electron counts.

An important feature of this paper is the extension of octahedral metal cluster chemical bonding models to infinite solid state systems. In this context the concept of an octahedral metal cluster repeating unit is most fundamental. In general, atoms shared by two or more such repeating units are partitioned equally between the repeating units. Electrons and orbitals from such shared atoms may not necessarily be partitioned equally but the sums of the electrons and the orbitals donated by the atom to all of the units sharing the atom in question must equal the total number of valence electrons and orbitals available from the neutral atom.

DISCRETE OCTAHEDRAL METAL CLUSTERS

Discrete octahedral metal clusters can be classified into the following three types (Table 1):

(1) Edge-localized: The chemical bonding manifold of an edge-localized metal octahedron is one-dimensional corresponding to the 1-skeleton[27] of the octahedron consisting of twelve two-center bonds along the twelve edges of the octahedron. This chemical bonding manifold requires 24 skeletal electrons and 24 internal orbitals corresponding to 4 internal orbitals for each vertex atom. Important examples of such edge-localized metal octahedra include the molybdenum (II) halide derivatives $Mo_6X_8L_6^{4+}$ such as "molybdenum dichloride," $Mo_6(\mu_3\text{-}Cl)_8Cl_2Cl_{4/2}$ (ref. 28) as well as the ternary molybdenum chalcogenides MMo_6S_8 (Chevrel phases).[29]

(2) Face-localized: The chemical bonding manifold of a face-localized metal octahedron is two-dimensional consisting of eight three-center bonds in the eight faces of the octahedron. This chemical bonding manifold requires 16 skeletal electrons and 24 internal orbitals corresponding to four internal orbitals for each vertex atom. Face-localized octahedra thus require the same number of skeletal orbitals but eight skeletal electrons less than edge-localized octahedra. Important examples of such face-localized metal

TABLE 1

THE TYPES OF CHEMICAL BONDING MANIFOLDS FOR DISCRETE OCTAHEDRAL METAL CLUSTERS

Bonding Type	Internal Orbitals from each Vertex Atom	Skeletal Bonding Manifold Dimensionalities	Examples[a]
Edge-localized	4	1 (i.e., 1-skeleton)	$Mo_6X_8L_6^{4+}$, "Mo_6Cl_{12}", Chevrel phases
Face-localized	4	2 (i.e., empty closed surface)	$Nb_6X_{12}L_6^{2+}$
Globally delocalized	3	2 (surface bonding) 3 (core bonding)	$Zr_6Cl_{12}Be$, $Zr_6Cl_{13}B$, $Zr_6Cl_{15}N$, $Rh_6(CO)_{16}$, $Os_6(CO)_{18}^{2-}$

(a) L refers to electron pair donor ligands (including lone electron pairs from halogens or chalcogens bridging to other octahedra); the Be, B, and N atoms in the Zr_6 clusters are located in the center of the Zr_6 octahedra.

octahedra include the niobium halide derivatives $Nb_6X_{12}L_6^{2+}$ such as the binary halide $Nb_6(\mu_2\text{-}Cl)_{12}Cl_{6/3}$ (= Nb_6Cl_{14})[30]

(3) Globally delocalized: The chemical bonding manifold of a globally delocalized metal octahedron is three-dimensional consisting of six two-center bonds delocalized in the surface of the octahedron and a single six-center core bond delocalized in the volume of the octahedron. This chemical bonding manifold requires 14 skeletal electrons and 18 internal orbitals corresponding to only three internal orbitals for each vertex atom.[2-5] Typical examples of globally delocalized octahedral clusters are the octahedral boranes and carboranes (e.g., $B_6H_6^{2-}$ and $C_2B_4H_6$) as well as octahedral metal cluster carbonyls (e.g., $Rh_6(CO)_{16}$ and $Ru_6(CO)_{17}C$). Globally delocalized octahedral early transition metal halide clusters include zirconium halide clusters containing an interstitial atom which have the general formula $Zr_6(\mu_2\text{-}Cl)_{12}ECl_{n-12}^{z+}$ (E = Be, B, C, N; z = 10-n+p_E where p_E is the number of valence electrons of the neutral interstitial atom E).[31]

Electron counting in discrete edge-localized octahedral metal clusters can be illustrated by using the molybdenum (II) halide derivatives generically represented as $Mo_6X_8L_6^{4+}$. The structures of these compounds consist of Mo_6 octahedra, a face-bridging (μ_3) halogen atom in each of the eight octahedral faces, and one bond from each molybdenum vertex to an external ligand (L), which may be a halogen atom bridging from another Mo_6 octahedron as in "molybdenum dichloride," $Mo_6(\mu_3\text{-}Cl)_8Cl_2Cl_{4/2}$.[28] The coordination polyhedron of each of the vertex molybdenum atoms is a C_{4v} 4-capped square antiprism with the external ligand L in the unique axial position, four bonds to face-bridging halogen atoms in the four equivalent medial positions, and the four internal orbitals in the four equivalent basal positions forming the two-center bonds with the adjacent molybdenum atoms in the same Mo_6 octahedron. An L-Mo vertex using four internal orbitals and thus five external orbitals is a (5)(2) - 6 - 2 = 2 electron acceptor (or -2 electron donor) after allowing for six electrons from the neutral molybdenum atom and two electrons from the neutral ligand L. This leads to the following electron-counting scheme[4]:

6 LMo vertices: (6)(-2) =	-12 electrons
8 μ_3-X bridges: (8)(5) =	40 electrons
+4 charge:	-4 electrons
Net skeletal electrons:	24 electrons

These 24 skeletal electrons are exactly the number required for an edge-localized octahedron having twelve two-center edge bonds as discussed above.

Electron counting in discrete face-localized octahedral metal clusters can be illustrated using the niobium halide clusters of the type $Nb_6X_{12}L_6^{2+}$

including the binary halide $Nb_6(\mu_2\text{-}Cl)_{12}Cl_{6/3}$ (= Nb_6Cl_{14}).[30] The structures of these compounds consist of Nb_6 octahedra, an edge-bridging (μ_2) halogen atom across each of the twelve octahedral edges, and one bond from each niobium vertex to an external ligand (L), which may be a halogen atom bridging from another Nb_6 octahedron such as in Nb_6Cl_{14}. The edge-bridged face-localized $Nb_6X_{12}L_6^{2+}$ are thus complementary to the face-bridged edge-localized $Mo_6X_8L_6^{4+}$ clusters discussed above. In the $Nb_6X_{12}L_6^{2+}$ clusters an L-Nb vertex using four internal orbitals and thus five external orbitals is a (5)(2) - 5 - 2 = 3 electron acceptor (or -3 electron donor) after allowing for five electrons from the neutral Nb atom and two electrons from the neutral ligand L. This leads to the following electron-counting scheme for $Nb_6X_{12}L_6^{2+}$:

6 LNb vertices: (6)(-3) =	-18 electrons
12 μ_2-X bridges: (12)(3) =	36 electrons
+2 charge:	-2 electrons
Net skeletal electrons:	16 electrons

These 16 skeletal electrons are exactly the number required for a face-localized octahedron with its eight three-center face bonds as discussed above.

Electron counting in discrete globally delocalized octahedral early transition metal halide clusters containing an interstitial atom can be illustrated by the zirconium chloride cluster $Zr_6Cl_{15}N$ containing an interstitial nitrogen atom in the center of a Zr_6 octahedron. In $Zr_6Cl_{15}N$ each zirconium vertex is bonded to five chlorine atoms. Four of these chlorine atoms (μ_2-Cl) bridge edges to a neighboring zirconium atom whereas the fifth chlorine atom bridges from another Zr_6 octahedron. This latter (external) chlorine may formally be regarded as a ligand (L) so that $Zr_6Cl_{15}N$ may be treated as $Zr_6Cl_{12}NL_6^{3+}$. The zirconium vertices clearly use five external orbitals for bonding to chlorine atoms making them (5)(2) - 4 - 2 = 4 electron acceptors (-4 electron donors). This leads to the following electron counting scheme for $Zr_6Cl_{12}NL_6^{3+}$ (= $Zr_6(\mu_2\text{-}Cl)_{12}NCl_{n-12}^{3+}$):

6 LZr vertices: (6)(-4) =	-24 electrons
12 μ_2-Cl Bridges: (12)(3) =	36 electrons
Interstitial N atom:	5 electrons
+3 charge:	-3 electrons
Net skeletal electrons	14 electrons

This is the correct electron count for a globally delocalized octahedron which has six two-center bonds delocalized in the surface of the octahedron and a single six-center core bond delocalized in the volume of the octahedron. Note that this bonding topology requires only three internal orbitals from each vertex atom meaning that each vertex zirconium atom has a manifold of only eight bonding orbitals, namely five external and three rather than four

internal orbitals. This corresponds to a 16-electron configuration similar to that found in a variety of stable zirconium compounds such as $(C_5H_5)_2ZrCl_2$. Also note that the presence of an interstitial atom in the center of an octahedral cluster favors a bonding topology containing a six-center core bond delocalized through the octahedral volume containing the interstitial atom rather than bonding topologies having only edge bonding in the octahedral 1-skeleton or face bonding in the octahedral surface.

INFINITE FUSION OF METAL OCTAHEDRA

The fusion of metal cluster octahedra can extend infinitely in a single dimension leading to chains of such octahedra, in two dimensions leading to graphite-like sheets constructed from metal octahedra, or in all three dimensions leading to the bulk metals themselves.[32] Examples of infinite chains of edge-fused metal cluster octahedra are found in the lanthanide halides of the stoichiometry M_2Cl_3 as exemplified by Gd_2Cl_3 (Figure 1).[33] Examples of two-dimensional infinite sheets of metal cluster octahedra are the graphite-like zirconium monohalides (Figure 2).[34] This section discusses electron and orbital bookkeeping in these one-dimensional and two-dimensional systems and implications of the resulting model for the structure and bonding in bulk metals, which represent the limiting case of infinite polyhedral fusion in all three dimensions.

Consider first the chains of edge-fused octahedra in Gd_2Cl_3 (Figure 1). These metal chains have both Gd_6 octahedral cavities (a^2b^4 in Figure 1) and Gd_4 tetrahedral cavities (a^2b^2 in Figure 1) with twice the number of tetrahedral cavities as octahedral cavities. A repeating octahedral Gd_6 unit in the chain can be represented as $Gd_2{}^aGd_{4/2}{}^b(\mu_3{}^{abb}\text{-}Cl)_4(\mu_2{}^{aa}\text{-}Cl)_{4/2}$. Both the axial (a in Figure 1) and bridging (b in Figure 1) gadolinium atoms are nine-coordinate and use five external orbitals each for bonds to chlorine atoms, four of which are in the same chain and the fifth ("external") halogen atom (not shown in Figure 1) is located in an adjacent chain of metal octahedra. Thus the gadolinium atoms each are (2)(5) - 3 - 2 = 5 electron acceptors (-5 electron donors) after allowing for the three electrons of the neutral gadolinium and an electron pair from the external halogen atoms. This leads to the following count of skeletal electrons and internal orbitals for an octahedral Gd_6 unit in Gd_2Cl_3 (= $Gd_2{}^aGd_{4/2}{}^b)(\mu_3{}^{abb} - Cl)_4(\mu_2{}^{aa} - Cl)_{4/2}$:

2 axial Gd: (2)(-5) =	-10 electrons	(8 orbitals)
4/2 axial Gd: (2)(-5) =	-10 electrons	(8 orbitals)
4 μ_3-Cl: (4)(5) =	20 electrons	
4/2 μ_2-Cl: (4/2)(3) =	6 electrons	
Total skeletal electrons and internal orbitals	6 electrons	(16 orbitals)

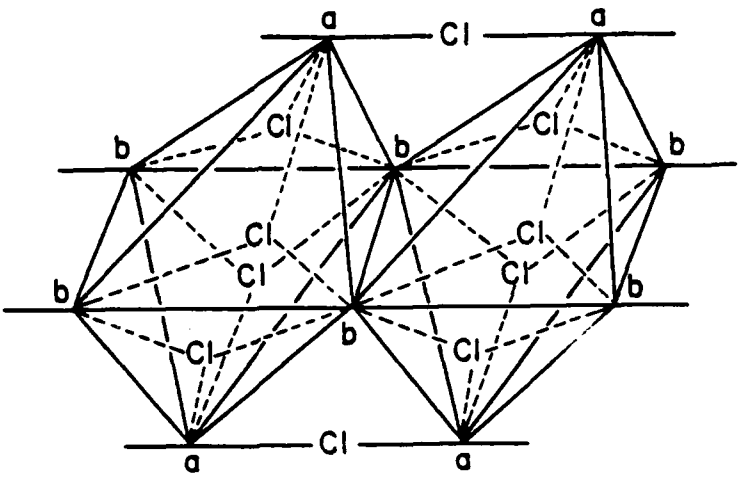


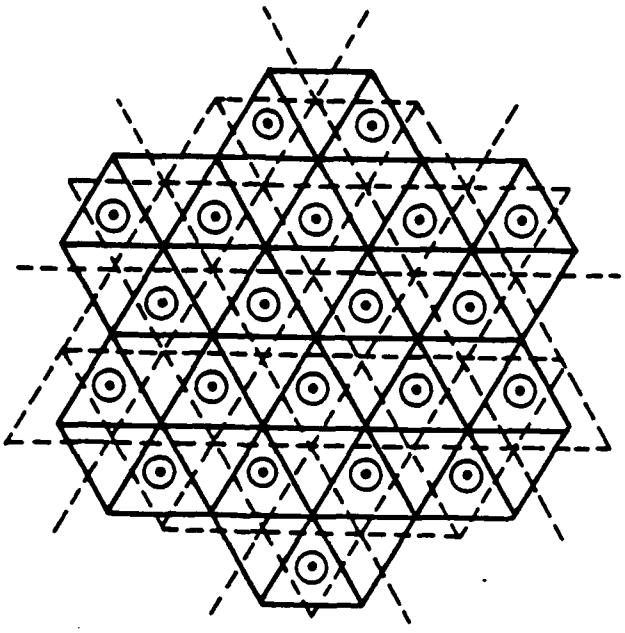
Fig. 1. Lanthanide halide structures (e.g. Gd_2Cl_3) based on edge-fused octahedra showing a unit of two octahedra. For clarity electron pair donation from halogens in other chains to each vertex atom is not shown.

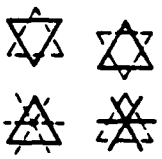
These skeletal electrons and internal orbitals can be used in the octahedral Gd_6 unit as follows:

1 6-center octahedral core bond (a^2b^4)	2 electrons	6 orbitals
2 4-center tetrahedral core bonds (a^2b^2)	4 electrons	8 orbitals
Total electrons and orbitals required	6 electrons	14 orbitals

The failure to use two of the available 16 orbitals in this bonding topology can correspond to the axial gadolinium atoms (two for each octahedral Gd_6 unit) having 16-electron rather than 18-electron configurations. In addition, the apparent tendency for multicenter core bonding in tetrahedral as well as octahedral cavities in even this one-dimensional infinite metal cluster contrasts with the edge-localized bonding always found in tetrahedral chambers in discrete metal clusters.[2,4,20] The closed shell electronic configuration of Gd_2Cl_3 is consistent with its semiconducting energy gap E_g of approximately 1 eV.[35]

Now consider the two-dimensional infinite sheets of metal octahedra as found in the graphite-like zirconium monohalides (Figure 2)[34] or the hydrogen-stabilized lanthanide monohalides of the stoichiometry HLnX.[36] The structures of these systems are constructed from two layers of hexagonal sheets of metal atoms which form both octahedral and tetrahedral cavities (Figure 2). There are twice as many tetrahedral as octahedral cavities in





Octahedral cavities

Tetrahedral cavities

Sites of μ_3-X atoms above and below the sheets

Fig. 2. A top view of a segment of the two stacked hexagonal sheets of metal atoms in the zirconium monohalide structure. The sheet indicated in dotted lines is below the sheet indicated in solid lines.

these infinite sheet structures as in the infinite chain structure of Gd_2Cl_3 (Figure 1) discussed above. The octahedral cavities each have six internal faces and two external faces; the external faces are capped by μ_3 face-bridging halogen atoms (Figure 2). Each metal vertex is shared by three octahedral cavities. The nine valence orbitals of each vertex metal atom are directed towards the vertices of a 4,4,4-tricapped trigonal prism and are partitioned into three external orbitals for bonds to face-bridging halogen atoms, three internal orbitals for core bonding in the three octahedral cavities meeting

at the metal vertex in question, and three internal orbitals for face bonding across the external faces of the tetrahedral cavities meeting at the metal vertex in question. A zirconium vertex in such a system thus uses three external orbitals and is an acceptor of (2)(3) - 4 = 2 skeletal electrons (i.e., a -2 skeletal electron donor) after allowing for the four valence electrons of a neutral zirconium atom. This leads to the following electron counting scheme for ZrCl (= $Zr_{6/3}(\mu_3\text{-}Cl)_2$):

6/3 Zr: (6/3)(-2) =	-4 electrons	(12 orbitals)
2 μ_3-Cl: (2)(5) =	10 electrons	
Total skeletal electrons and orbitals	6 electrons	(12 orbitals)

These six skeletal electrons and twelve internal orbitals can be used for the following bonding topology based on a single repeating $Zr_{6/3}(\mu_3\text{-}Cl)_2$ octahedral unit:

1 6-center octahedral core bond	2 electrons	(6 orbitals)
2 3-center face bonds across external faces of tetrahedral cavities	4 electrons	(6 orbitals)
Total electrons and orbitals required	6 electrons	(12 orbitals)

Note that in the two-dimensional infinite sheets of ZrCl as in the one-dimensional infinite chains of Gd_2Cl_3 there are two tetrahedral cavities for each octahedral cavity and single multicenter bonds for each of these cavities, both tetrahedral and octahedral.

Now consider bulk metals as infinite arrays of fused octahedra in all three dimensions. The structures can be visualized as an infinite stacking of the hexagonal metal sheets in Figure 2 into the third dimension perpendicular to the sheets. In frequently encountered metallic structures such as the cubic close packed structures there are two tetrahedral cavities for each octahedral cavity analogous to the infinite one-dimensional edge-fused metal octahedra chains (e.g., Gd_2Cl_3 in Figure 1) and infinite two-dimensional edge-fused metal octahedra sheets (e.g., ZrCl in Figure 2) discussed above. In a bulk metal all of the valence orbitals of each metal atom are internal orbitals. Since each metal atom is shared by six octahedral cavities and since an octahedral cavity is formed by six metal atoms, the number of valence electrons for each octahedral cavity is equal to the number of valence electrons of the metal. Formation of one multicenter bond each in each octahedral cavity and in the two tetrahedral cavities for each octahedral cavity requires six electrons per octahedral cavity corresponding to a metal atom with six valence electrons such as chromium, molybdenum, or tungsten. This correlates with the experimental observation of maximum heat of

atomization (i.e., maximum stability of the metal lattice) for the group 6 metal tungsten[37] in the 5d transition metal series as well as the role of the transition metal divide[38] at the group 6 metals in determining the composition, structure, and properties of certain transition metal alloys such as the beta tungsten phases. In the 3d and 4d transition metal series the correlations are not quite as good since the maximum heats of atomization are found for the group 5 metals vanadium and niobium rather than the corresponding group 6 metals chromium and molybdenum, respectively[37]; this may be related to the s-d shear hypothesis of Stone.[38]

SUPERCONDUCTORS

The graph theory derived method for the study of the chemical bonding topology of metal clusters can also be extended to superconducting materials. In this connection Vandenberg and Matthias[22] have shown that most high temperature superconductors contain discrete metal clusters in this crystal lattices thereby suggesting the relevance of this approach.

One class of superconductors of particular interest consists of ternary molybdenum chalcogenides, commonly known as Chevrel phases.[29,39] These phases were the first superconducting ternary systems found to have relatively high critical temperatures[40] reaching 15 K for $PbMo_6S_8$. In addition the upper critical field of $PbMo_6S_8$ ($H_{c2} \approx 60T$) is the highest value observed for any class of superconductors.[41,42]

The most important type of Chevrel phases have the general formulas $M_nMo_6S_8$ and $M_nMo_6Se_8$ (M = Ba, Sn, Pb, Ag, lanthanides, Fe, Co, Ni, etc.). The basic building blocks of their structures are Mo_6S_8 (or Mo_6Se_8) units containing a bonded Mo_6 octahedron (Mo-Mo distances in the range 2.67 to 2.78 Å) with a sulfur atom capping each of the eight faces. This leads to an Mo_6 octahedron within an S_8 cube. Each (neutral) sulfur atom of the S_8 cube functions as a donor of four skeletal electrons to the Mo_6 octahedron within that S_8 cube leaving an electron pair to function as a ligand to a molybdenum atom in an adjacent Mo_6 octahedron. Maximizing this sulfur electron pair donation to the appropriate molybdenum atom in the adjacent Mo_6 octahedron results in a tilting of the Mo_6 octahedron by about 25° within the cubic array of the other metal atoms M.[43] These other metal atoms M furnish electrons to the Mo_6S_8 units allowing them to approach but not attain the $Mo_6S_8^{4-}$ closed shell electronic configuration. This corresponds to a partially filled conduction band. Electronic bridges between individual Mo_6 octahedra are provided by interoctahedral metal-metal interactions (nearest interoctahedral Mo-Mo distances are in the range 3.08 to 3.49 Å for Mo_6S_8 and Mo_6Se_8 derivatives).[29]

The $Mo_6S_8^{4-}$ closed shell electronic configuration for the fundamental

Chevrel phase building block is isoelectronic with that of the $Mo_6X_8L_6^{4+}$ halides discussed above remembering that each molybdenum vertex receives an electron pair from a sulfur atom of an adjacent Mo_6S_8 unit and thus may be treated as an LMo vertex. This leads to the following electron counting scheme for the closed shell $Mo_6S_8^{4-}$ unit:

6 LMo vertices: (6)(-2) =	-12 electrons
8 μ_3-S bridges: (8)(4) =	32 electrons
-4 charge	4 electrons
Total skeletal electrons	24 electrons

These 24 skeletal electrons are again the exact number required for an edge-localized octahedron having two-center bonds along each of the 12 edges. Note the analogy between the chemical bonding topology in $Mo_6S_8^{4-}$ and that in $Mo_6X_8L_6^{4+}$ discussed above.

The Chevrel phases include not only species constructed from discrete Mo_6S_8 (or Mo_6Se_8) octahedra but also species constructed from Mo_9S_{11}, $Mo_{12}S_{14}$, and $(Mo_6S_6)_\infty$ units formed from the fusion of octahedra by sharing triangular faces. This fusion process may be regarded as analogous to the formation of polycyclic aromatic hydrocarbons from the fusion of hexagons by sharing edges. This suggests the classification of fused molybdenum octahedra by the trivial name of the polycyclic benzenoid hydrocarbon having an analogous configuration of its planar hexagon building blocks (Figure 3). A similar scheme has also been used to classify rhodium carbonyl clusters having related structures based on face fused octahedra.[20,21] In the case of the fused molybdenum sulfide octahedra in Figure 3 only the linearly fused species are known analogous to the linear polyacenes (benzene, naphthalene, anthracene, tetracene, pentacene, etc.).

The molybdenum atoms in the fused octahedra of Figure 3 are of two types, inner and outer. Outer molybdenum atoms are similar to those in the discrete octahedral Mo_6S_8 building blocks discussed above. They thus use four internal orbitals and receive an electron pair from a sulfur atom of an adjacent metal cluster unit (indicated by arrows in Figure 3). The inner molybdenum atoms (circled in Figure 3) use six internal orbitals and do <u>not</u> receive an electron pair from a sulfur atom of an adjacent metal cluster. They are therefore zero electron donors, i.e. (3)(2) - 6 - 0 = 0. Edges connecting pairs of inner molybdenum atoms are bridged by sulfur atoms but these sulfur atoms also bond to one molybdenum atom in each adjacent Mo_3 triangle ("above" and "below" in Figure 3) so that they function as μ_4 sulfur atoms and donors of four skeletal electrons to their own cluster units. Thus all sulfur atoms in the species depicted in Figure 3 may be regarded as four-electron donors when considered as neutral ligands. Electron and orbital counting arguments summarized in detail elsewhere[23] suggest a combination of face-localized

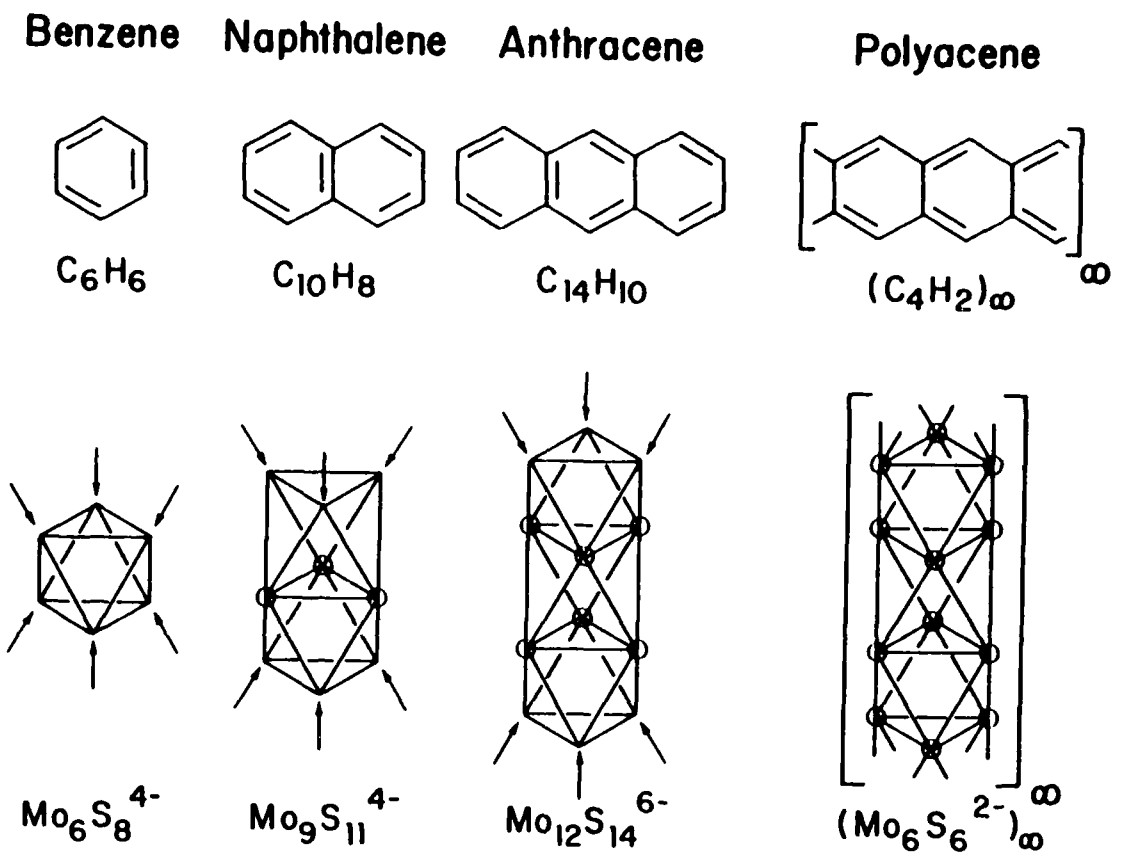


Fig. 3. Analogy between the fusion of molybdenum octahedra in ternary molybdenum sulfide structures and the fusion of benzene rings in planar polycyclic aromatic hydrocarbons. Uncircled vertices are outer molybdenum atoms and circled vertices are inner molybdenum atoms. Arrows indicate sites of coordination with sulfur atoms of adjacent metal cluster units. Sulfur atoms are omitted for clarity. Similar structural units are present in analogous molybdenum selenides and tellurides.

and edge-localized bonding in Mo_6 octahedra formed from a triangle of outer molybdenum atoms and a triangle of inner molybdenum atoms (e.g., both octahedral cavities in the naphthalene analogue $Mo_9S_{11}^{4-}$) but globally delocalized bonding in Mo_6 octahedra formed only from inner molybdenum atoms (e.g., the central octahedral cavity in the anthracene analogue $Mo_{12}S_{14}^{6-}$).

The limit to the face-sharing fusion of molybdenum octahedra is the infinite linear polyacene analogue $(Mo_6S_6^{2-})_\infty$ (Figure 3) known in a number of derivatives $[M_2Mo_6S_6]_\infty$ (M = K, Rb, Cs) as well as the selenium analogues $[M_2Mo_6Se_6]_\infty$ (M = Na, K, Rb, Cs, Tl, Ag) and the tellurium analogues $[M_2Mo_6Te_6]_\infty$ (M = Rb, Cs, In, Tl).[44,45] All molybdenum atoms in these infinite chains of face-fused octahedra are inner molydenum atoms and none of the chalcogens bridge to other chains so that there are no close contacts between the different chains. In accord with this structure these systems function as pseudo-one-dimensional metals with strongly anisotropic conductivities several hundred times larger parallel to the chains of octahedra relative to the perpendicular directions.[44,46] The $Mo_{6/2}S_{6/2}^{-}$ octahedra serving as building blocks for these $[M_2Mo_6S_6]_\infty$ derivatives and their selenium and tellurium analogues have 13 skeletal electrons, i.e. none from the (inner) molybdenum vertices, 12 [= (6/2)(4)] from the three (= 6/2) sulfur atoms, and 1 from the -1 charge. These 13 skeletal electrons for each $Mo_{6/2}S_{6/2}^{-}$ unit are one less than the 14 skeletal electrons required for the corresponding octahedral cavity to be globally delocalized (2n + 2 = 14 for n = 6). These holes in the closed shell electronic configurations for globally delocalized $(Mo_6S_6^{-2})_\infty$ provide a mechanism for electronic conduction along the chains of face fused octahedra. Peierls distortions[47,48] leading to alternately long and short spaces between the Mo_3X_3 (X = S, Se, Te) units in the chains of fused octahedra appear to be relatively unfavorable but have been suggested[45,49] to account for the broad metal-semiconductor transitions in the ternary molybdenum tellurides $[M_2Mo_6Te_6]_\infty$ (M = Rb, Cs).

Another interesting class of high temperature superconductors consists of the ternary lanthanide rhodium borides, $LnRh_4B_4$ (Ln = certain lanthanides such as Nd, Sm, Er, Tm, Lu),[50,51] which exhibit significantly higher superconducting transition temperatures than other types of metal borides. These rhodium borides have a structure consisting of electronically linked Rh_4 tetrahedra and thus provide further support of the general idea of Vandenberg and Matthias[22] that most high temperature superconductors contain discrete metal clusters in their crystal lattices. The topology of an individual Rh_4B_4 unit in these ternary borides is that of a tetracapped tetrahedron of T_d local symmetry in which the four degree 6 vertices correspond to rhodium atoms and the four degree 3 vertices correspond to boron atoms. Furthermore, a tetracapped tetrahedron is topologically equivalent to a cube

with diagonals drawn across each of its six faces in such a way to preserve tetrahedral (T_d) overall symmetry. The diagonals of such a cube correspond to six Rh-Rh bonds (average length 2.71 Å in YRh_4B_4)[52] and the edges of such a cube correspond to twelve Rh-B bonds (average length 2.17 Å in YRh_4B_4).[52] The ratio between these two lengths, namely 2.71/2.17 = 1.25, is only about 13% less than the $\sqrt{2}$ = 1.414 ratio of these lengths in an ideal cube. This suggests that the Rh_4B_4 building blocks can be approximated by a cube in the three-dimensional lattice. The Rh-Rh distances of 2.71 Å in these Rh_4B_4 units are essentially identical to the mean Rh-Rh distance in the discrete molecular tetrahedral rhodium cluster[53] $Rh_4(CO)_{12}$ regarded as a prototypical example of an edge-localized tetrahedron.[2,4]

The boron and rhodium atoms in $LnRh_4B_4$ have four and nine valence orbitals, respectively. All of these valence orbitals are used to form two-center bonds leading to an edge-localized structure. The four bonds formed by a boron atom are as follows:

(1) Three bonds to rhodium atoms in the same Rh_4B_4 cube (average Rh-B distance 2.17 Å in YRh_4B_4).

(2) One bond to the nearest boron atom in an adjacent Rh_4B_4 cube (B-B distance 1.86 Å in YRh_4B_4) thereby leading to discrete B_2 units in the structure.

The nine bonds formed by a rhodium atom are as follows:

(1) Three bonds to rhodium atoms in the same Rh_4 tetrahedron (average Rh-Rh distance 2.71 Å in YRh_4B_4).

(2) Three bonds to boron atoms in the same Rh_4B_4 cube (average Rh-B distance 2.17 Å in YRh_4B_4).

(3) One bond to the nearest rhodium atom in another Rh_4B_4 cube in the same sheet of such cubes (Rh-Rh distance 2.68 Å in YRh_4B_4).

(4) Two bonds to the next nearest rhodium atoms in adjacent Rh_4B_4 cubes (Rh-Rh distances 3.14 Å in YRh_4B_4).

In deriving the chemical bonding topology each boron atom is considered to have three internal orbitals and one external orbital and is therefore a donor of two skeletal electrons since one of the three boron valence electrons is needed for the B-B bond using its external orbital. Similarly each rhodium atom has six internal orbitals and three external orbitals and is therefore a donor of six skeletal electrons since three of the nine rhodium valence electrons are needed for the three external Rh-Rh bonds formed by a given rhodium atom.

From these considerations a neutral Rh_4B_4 unit in the $LnRh_4B_4$ borides can be shown to have 32 skeletal electrons as follows:

4 Rh vertices: (4)(6) =	24 electrons
4 B vertices: (4)(2) =	8 electrons
Total skeletal electrons for each Rh_4B_4 unit:	32 electrons

Since a tetracapped tetrahedron or the topologically equivalent cube with six diagonals has 18 edges corresponding to six Rh-Rh bonds and twelve Rh-B bonds as outlined above, a closed shell edge-localized Rh_4B_4 unit requires (2)(18) = 36 skeletal electrons corresponding to the tetraanion $Rh_4B_4^{4-}$. Since the lanthanides also present in the lattice form tripositive rather than tetrapositive ions, the $LnRh_4B_4$ borides must be $Ln^{3+}Rh_4B_4^{3-}$ with the $Rh_4B_4^{3-}$ anion having one electron less than the closed shell electronic configuration $Rh_4B_4^{4-}$. This electron deficiency provides a partially filled conduction band leading to facile electron transport and high electronic conductivity.

The chemical bonding topologies of both the Chevrel phases MMo_6S_8 and the ternary lanthanide rhodium borides both consist of edge-localized discrete metal polyhedra (Mo_6 octahedra and Rh_4 tetrahedra, respectively) linked into a three-dimensional structure both through other atoms (sulfur and boron, respectively) and through interpolyhedral metal-metal interactions. This leads naturally to the concept of <u>porous delocalization</u>. Thus the bonding in a polyhedron with edge-localized bonding is porous in contrast to the dense bonding in a polyhedron with globally delocalized bonding. In other words porous chemical bonding uses a one-dimensional chemical bonding manifold[54] corresponding to the 1-skeleton[27] of the polyhedron in contrast to dense chemical bonding which uses a three-dimensional chemical bonding manifold[54] involving the whole volume of the polyhedron. An interesting refinement of the idea of Vandenberg and Matthias[22] arising from this analysis of the chemical bonding topology of both the Chevrel phases and the ternary lanthanide rhodium borides is the conjecture that a porously delocalized three-dimensional network consisting of electronically linked polyhedral metal clusters having edge-localized chemical bonding leads to superconducting systems having relatively high critical temperatures and magnetic fields. Thus the porosity of the chemical bonding in these systems makes their superconductivity more resistant to magnetic fields and temperature than that of densely delocalized systems such as pure metals. This idea appears to be related to the suggestion[55] that the high critical field of the Chevrel phases arises from a certain localization of the conduction electron wave function on the Mo_6 clusters leading to an extremely short mean free path and/or a low Fermi velocity corresponding to a small B.C.S. coherence length.

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